STO - Gaussian Overlap Notes

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1. Slater Type Orbitals

Slater Type Orbitals (STO)[1] in the atomic orbital (AO) basis are used in semiempirical methods based on Neglect of Differential Diatomic Overlap (NDDO) such as AM1. STO are given by:

$$\chi_{nlm}(\vec{r}_A) = N_n(\xi)\, r_A^{n-1} e^{-\xi r_A}\, Y_{lmn}(\theta_A, \phi_A), \tag{1}$$

with normalization:

$$N_n(\xi) = \left(\frac{(2\xi)^{2n+1}}{(2n)!} \right)^{1/2}, \tag{2}$$

where ξ is the orbital exponent (parameter depending on the given orbital and semiempiric method such as AM1), n is the principal quantum number, $\vec{r}_A$ is the correspondent distance to the nucleus, and $Y_{lmn}(\theta_A, \phi_A)$ are the normalized real harmonics.[2] In these notes we'll only consider s and p types of orbitals:

$$(l=0, m=0) \longrightarrow |ns\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \frac{1}{\sqrt{4\pi}}, \tag{3}$$

$$(l=0, m=1) \longrightarrow |np_x\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}}\, \frac{x}{r}, \tag{4}$$

$$\frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}}\, \frac{y}{r}, \tag{5}$$

$$|np_z\rangle = \frac{(2\xi)^{n+1/2}}{((2n)!)^{1/2}}\, r^{n-1} e^{-\xi r} \sqrt{\frac{3}{4\pi}}\, \frac{z}{r}, \tag{6}$$

where x, y, and the Cartesian coordinates in the coordinate system centered in the corresponding atom.

2. Slater Type Orbitals

A primitive Cartesian Gaussian Orbital is typically writen as:

$$\phi^{(A)}_{l_x l_y l_z}(\vec{r}, \alpha) = N(l_x, l_y, l_z, \alpha)\, x^{l_x} y^{l_y} z^{l_z} e^{-\alpha r^2}, \tag{7}$$

where the total angular degree is $l = l_x + l_y + l_z$, α is the Gaussian exponent, and the normalization factor is given by:

$$N(l_x, l_y, l_z, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \sqrt{\frac{(8\alpha)^{l_x+l_y+l_z}\, l_x!\, l_y!\, l_z!}{(2l_x)!\,(2l_y)!\,(2l_z)!}}, \tag{8}$$

For s type GTO we get:

$$\phi_s(\vec{r}, \alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}, \tag{9}$$

while for p type GTO we get:

$$\phi_{p_x}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}}\, x e^{-\alpha r^2}, \tag{10}$$

$$\phi_{p_y}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}}\, y e^{-\alpha r^2}, \tag{11}$$

$$\phi_{p_z}(\vec{r}, \alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}}\, z e^{-\alpha r^2}, \tag{12}$$

3. Overlap Integrals

For deriving tractable equations for the overlap integrals we'll use the following identity (Gauss Transform):

$$e^{-\varrho r} = \frac{\varrho}{\sqrt{\pi}} \int_0^\infty u^{-3/2} e^{-\varrho^2/4u} e^{-ur^2}\, du, \tag{13}$$

representing the Slater exponential as a continuos superposition of Gaussians.[3] We'll also use the Gaussian product theorem:

$$e^{-ur_A^2} e^{-\alpha r_B^2} = \exp(-\mu R^2) \exp\left[-(u+\alpha)(r-P)^2\right], \tag{14}$$

where:

$$P = \frac{uA + \alpha B}{u + \alpha}, \tag{15}$$

and:

$$\mu = \frac{u\alpha}{u+\alpha}, \tag{16}$$

3.1 s-s

Evaluating eq.(3) and eq.(9) in displaced atomic centers $\vec{A}$ and $\vec{B}$ such that $\vec{R} = \vec{A} - \vec{B}$, and $R = |\vec{R}|$, using the Gauss Transform eq.(13), swapping the integration operators, solving for the spatial integral, and using the identity:

$$r_A^{n-1} e^{-\xi r_A} = \left(-\frac{\partial}{\partial \xi}\right)^{n-1} e^{-\xi r_A}, \tag{17}$$

we get:

$$S_{ss}^{(n)}(R, \xi, \alpha) = N_{n0}(\xi) N_s(\alpha) \pi \, 2^{-n} \int_0^\infty \frac{u^{-\frac{(n+1)}{2}}}{(u+\alpha)^{3/2}} e^{-\frac{u\alpha}{u+\alpha}R^2} e^{-\xi^2/4u} H_n\left(\frac{\xi}{2\sqrt{u}}\right) du, \tag{18}$$

where:

$$N_{n0}(\xi) = \left(\frac{(2\xi)^{2n+1}}{(2n)!}\right)^{1/2} \frac{1}{\sqrt{4\pi}}, \tag{19}$$

and:

$$N_s(\alpha) = \left(\frac{2\alpha}{\pi}\right)^{3/4}, \tag{20}$$

and H_n is the Hermite polynomial.

3.2 s-p

Analogously, by using eqs. (10-12), we get:

$$S_{s\text{-}p_k}^{(n)} = N_{n0}(\xi) N_p(\alpha) \pi \, 2^{-n} R_k \int_0^\infty \frac{u^{-\frac{(n-1)}{2}}}{(u+\alpha)^{5/2}} e^{-\frac{u\alpha}{u+\alpha}R^2} e^{-\xi^2/4u} H_n\left(\frac{\xi}{2\sqrt{u}}\right) du, \tag{21}$$

where:

$$N_p(\alpha) = \frac{(2\alpha)^{5/4}}{\pi^{3/4}}, \tag{22}$$

3.3 p-s

Analogously we get:

$$S^{(n)}_{p_k-s} = -N_{STO,p}(\varrho) N_s(\alpha) \pi \alpha\, 2^{-(n-1)} R_k \int_0^\infty \frac{u^{-n/2}}{(u+\alpha)^{5/2}} e^{-\frac{u\alpha}{u+\alpha} R^2} e^{-\varrho^2/4u} H_{n-1}\left(\frac{\varrho}{2\sqrt{u}}\right), \tag{23}$$

where:

$$N_{STO,p}(\varrho) = \left(\frac{(2\varrho)^{2n+1}}{(2n)!}\right)^{1/2} \sqrt{\frac{3}{4\pi}}, \tag{24}$$

3.4 p-p

Using eqs. (4-6) and eqs. (10-12) we get:

$$S^{(n)}_{p_k-p_l}(\varrho) = N_{STO,p}(\varrho) N_p(\alpha) \pi\, 2^{-(n-1)} \int_0^\infty \frac{u^{-n/2}}{(u+\alpha)^{3/2}} e^{-\frac{u\alpha}{u+\alpha} R^2} e^{-\varrho^2/4u} H_{n-1}\left(\frac{\varrho}{2\sqrt{u}}\right) \times$$

$$\times \left[\left(-\frac{\alpha}{u+\alpha} R_k\right)\left(\frac{u}{u+\alpha} R_l\right) + \frac{\delta_{kl}}{2(u+\alpha)}\right] du, \tag{25}$$

4. Quadrature

In order to calculate numerically the relevant integrals, let's introduce the following substitution:

$$u = \frac{\varrho^2}{4t}, \tag{26}$$

$$du = -\frac{\varrho^2}{4t^2} dt, \tag{27}$$

for which the integrals become:

$$\int_0^\infty e^{-t} G(t) dt, \tag{28}$$

where:

$$G(t) = t^{-(a+2)} \left(1 + \frac{4t\alpha}{\xi^2}\right)^{-b} \exp\left[-\frac{\alpha R^2 \xi^2 t}{4t\alpha + \xi^2}\right] H_m(\sqrt{t})\, A\left(\frac{\xi^2}{4t}, R\right), \tag{29}$$

where:

	s-s	s-p_k	p_k-s	p_k-p_l
N	$N_{n0}(\xi) N_s(\alpha) \pi\, 2^{-n}$	$N_{n0}(\xi) N_p(\alpha) \pi\, 2^{-n} R_k$	$-N_{STO,p}(\xi) N_s(\alpha) \pi \alpha\, 2^{-(n-1)} R_k$	$N_{STO,p}(\xi) N_p(\alpha) \pi\, 2^{-(n-1)}$
a	$-\frac{(n+1)}{2}$	$-\frac{(n-1)}{2}$	$-\frac{n}{2}$	$-\frac{n}{2}$
b	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{3}{2}$
m	n	n	$n-1$	$n-1$
$A(t,R)$	1	1	1	$-\frac{4\alpha\xi^2 t}{(4\alpha t+\xi^2)} R_k R_l + \frac{2t}{4\alpha t + \xi^2} \delta_{kl}$

Finally, the integral in eq. (28) can be calculated by means of the Gauss-Laguerre node/weights:

$$\int_0^\infty e^{-t} G(t)\, dt = \sum_{i=1}^{N} w_i G(t_i), \tag{30}$$

Tip: Use $N=32$ as a default and check against 48 and 64 for convergence when developing

References

[1] James J. P. Stewart, "Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and applications to 70 elements", J. Mol. Model. (2007) 13: 1173-1213.

[2] Miguel A. Blanco, M. Flórez, M. Bermejo, "Evolution of rotation matrices in the basis of real spherical harmonics," Journal of Molecular Structure (Theochem) 419 (1997) 19-27.

[3] André Severo Pereira Gómez, Rogelio Custodio, "Exact Gaussian Expansions of Slater Type Atomic Orbitals", Journal of Computational Chemistry, 23.10 (2007) 1007-1012.